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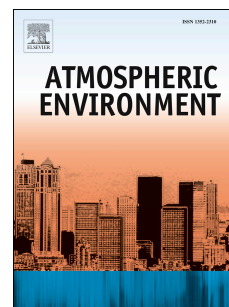
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Characterization of Ambient PM_{2.5} at a Pollution Hotspot in New Delhi, India and Inference of Sources

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ABSTRACT

Ambient PM_{2.5} samples were collected at a high-traffic location (summer and winter 2013) and characterized for a large suite of elemental and organic markers. Concentrations were found to exceed the Indian PM_{2.5} air quality standard on several occasions, especially in the winter. Winter concentrations of several individual tracer species were several fold higher compared to summer, particularly for some PAHs and trace metals. Enrichment factors relative to crustal material showed significant enrichment for elements such as Ti, Sb, Pb and As, although Ba, often used as a marker for non-exhaust emissions from traffic was not found to be enriched appreciably. Crustal material was found to be an important contributor in the summer (14.3%), while wood burning (23.3%), nitrates (12.4%) and chlorides (12.3%) were found to be major contributors in winter. The contribution of road traffic exhaust emissions was estimated to be 18.7% in summer and 16.2% in winter. Other combustion sources (wood and other biomass/waste/coal) were found to be a significant source in winter, and contribute to the higher concentrations. Secondary sulphates, nitrates and chloride (the latter two in winter) and organic matter also contribute substantially to PM_{2.5} mass.

Keywords: Molecular markers; traffic, India; mass closure; particulate matter

1. INTRODUCTION

Given the rapid rates of urbanization in Indian cities, air pollution is increasingly becoming a critical threat to the environment and to the quality of life among the urban population in India. Particulate matter (PM) concentrations are often found to exceed the Indian National Ambient Air Quality Standards (NAAQS) and recent studies have identified PM as one of the key public health risks, particularly in urban areas (Lim et al., 2012; Guttikunda and Goel, 2013; Trivedi et al., 2014). The primary sources of air pollution in India have been identified as vehicular emissions, industrial emissions, coal combustion, biomass burning, road dust and waste burning, construction activities, oil combustion and sea salt (Chowdhury et al., 2007; CPCB, 2010; Guttikunda and Calori, 2013; Gargava et al., 2014). An overview of PM sources is presented in Guttikunda et al. (2014).

There is a growing body of literature on source apportionment of PM in India which has used receptor modelling with both elements and organic markers, and a detailed review of source apportionment studies in India is presented in Pant and Harrison (2012). A large number of studies have focused on total suspended particulate matter (TSP) and PM₁₀ but there is an increasing number of studies focused on fine PM (aerodynamic diameter <2.5 µm) (Chowdhury et al., 2007; Tiwari et al., 2009; Chakrobarty and Gupta, 2010; Khare and Baruah, 2010; Gummeneni et al., 2011; Joseph et al., 2011). In terms of geographic distribution across the country, most studies focus on big cities such as Delhi (Balachandran et al., 2000; Khillare et al., 2004; Srivastava and Jain, 2007; Tiwari et al., 2009; Khillare and Sarkar, 2012; Trivedi et al., 2014), Mumbai (Kumar et al., 2001; Chelani et al., 2008; Kothai et al., 2008), Chennai (Srimuruganandam and Shiva Nagendra, 2011), Hyderabad (Gummeneni et al., 2011; Guttikunda et al., 2013) and Kolkata (Gupta et al., 2007; Kar et al., 2010). The Central Pollution Control Board (CPCB) also conducted a detailed dispersion and receptor modelling analysis in six cities across India (CPCB, 2010). In comparison, there are very few analyses in smaller cities/towns (e.g. Mouli et al., 2006; Kulshrestha et al., 2009;

Chakrobarty and Gupta, 2010; Masih et al., 2010; Giri et al., 2013). Some recent work focused on unique sources (Chakrobarty et al., 2013; Deka and Hoque, 2014; Kirillova et al., 2014; Srinivas and Sarin, 2014).

A majority of the PM source apportionment studies have been conducted using trace element markers (Balachandran et al., 2000; Kumar et al., 2001; Kothai et al., 2008) and in some cases, inorganic tracers have been used in conjunction with organic and elemental carbon (Gupta et al., 2007; Tiwari et al., 2009; Chelani et al., 2010; Sharma et al., 2013). The use of organic molecular markers for PM source apportionment has only been reported in recent years (Chowdhury et al., 2007; Fu et al., 2010; Masih et al., 2010; Giri et al., 2013; Herlekar et al., 2012; Li et al., 2014). In a comprehensive review on receptor modelling of PM in India, several gaps were highlighted including the need for detailed analyses using organic markers, focus on fine particles ($PM_{2.5}$), and the need to characterize the contribution of secondary sources to ambient PM concentrations (Pant and Harrison, 2012).

Delhi is one of the most polluted cities across the world and concentrations of air pollutants are often found to exceed the NAAQS. Delhi is reported to have 29 planned industrial areas and 5 factory complexes with a range of industries including food and beverages, metal and alloys, leather and leather products, chemicals, paper etc. (Delhi Statistical Handbook, 2013). Delhi has two coal thermal power plants and four natural gas power plants and the sulphur content in the coal used in power plants in Delhi typically ranges between 0.35% and 0.50% (Chowdhury et al., 2007). Indian coal is typically high in ash content. Diesel is used for both road transport (cars, utility vehicles, heavy duty vehicles [HDVs]) and industry (power back-up, mobile phone towers, miscellaneous) while gasoline is mostly used for road transport. Public transport in the city runs on compressed natural gas [CNG] while private vehicles run on diesel, gasoline, CNG and liquefied petroleum gas [LPG]. A number of brick kilns are also reported to operate in areas around Delhi (Guttikunda and

Calori, 2013). A range of different cooking fuels are used in Delhi including LPG, kerosene, firewood, cow dung cake, coal, crop residues, biogas and electricity with nearly 90% of households using LPG (Delhi Statistical Handbook, 2013). Estimated source contributions from the different sectors are described in Sahu et al. (2011a) and Guttikunda and Calori (2013). While on one hand, Sahu et al. (2011a) reported road transport as the biggest contributor to $PM_{2.5}$ emissions (30.25 Gg/yr) followed by residential emissions (18.65 Gg/yr), dust (18.35 Gg/yr) and industry (16.29 Gg/yr); Guttikunda and Calori (2013) identified transport, power plants and domestic emissions as the three biggest contributors. Several studies have been undertaken for source apportionment of suspended particulate matter (SPM), PM_{10} and $PM_{2.5}$ using receptor modelling in Delhi and a majority of those have used methods such as principal component analysis (PCA), PCA-MLR (multiple linear regression), diagnostic ratio, enrichment factor etc. However, several recent studies have used positive matrix factorization (PMF) and chemical mass balance (CMB) models for source apportionment. A large percentage of the PM has been attributed to vehicular emissions, road dust, coal combustion and domestic emissions in several studies (Balachandran et al., 2000; Khillare et al., 2004; Chowdhury et al., 2007; Sharma et al., 2007; Chelani et al., 2010; Tiwari et al., 2013). Goyal et al. (2010) have reported diesel vehicles to contribute nearly 28% of the total PM in Delhi. Other sources identified for PM emissions in Delhi include industrial emissions, open refuse burning and construction (Khillare et al., 2004; Mönkönnen et al., 2004; CPCB, 2010; Khillare and Sarkar, 2012; Guttikunda and Calori, 2013). Most receptor modelling studies, however, have focused on characterization of elemental, and in some case ionic species and PAHs, and there is a lack of studies with detailed characterization of molecular marker species in $PM_{2.5}$.

The objective of the current study was to conduct detailed chemical characterization of ambient $PM_{2.5}$ and to assess source contributions to $PM_{2.5}$ including primary and secondary sources.

2. MATERIALS AND METHODOLOGY

2.1 Sampling Location

Mathura Road is one of the major arterial roads in Delhi with an average traffic flow of 170,000 vehicles per day and a modal split shown in Figure 1. Other sources of PM include residential burning and an industrial hub about three kilometres from the sampling site (Okhla Industrial Area). Trucks are not allowed between 07:30 to 11:00 and 17:00 to 21:30 while buses, light duty vehicles (LDVs) and two and three wheelers are not restricted (Delhi Police, 2014). It is important to note that Bharat Standard IV (BS-IV, 50 ppm sulphur) standards are applicable to the vehicles within Delhi; vehicles from outside Delhi are often BS-III (equivalent of Euro III, 350 ppm sulphur).

The samplers were placed at a height of two meters from ground level at a distance of 50 meters from the road. Traffic emissions are the most prominent source. Other sources include biomass combustion in the low-income housing close to the sampling site, emissions from the industrial units located at a distance of ~3 kilometres from the sampling site and a power plant.

New Delhi has a sub-tropical climate with hot summers (April-June) and moderately cold winter (November to January). Typically, S-SW winds are prevalent in summer and N-NW winds are prevalent in winter (Yadav and Rajamani, 2006). During the summer sampling period (June 15-30, 2014), the average temperature and relative humidity (RH) were recorded as $31.4 \pm 4.02^{\circ}\text{C}$ and $67.5 \pm 20.5\%$ respectively while during the winter sampling period (December 15, 2013-January 15, 2014), the average temperature and RH were recorded as $13.4 \pm 2.7^{\circ}\text{C}$ and $80.8 \pm 8.1\%$ respectively. During the sampling period in winter, fog/haze was reported on most days with calm wind conditions. Average rainfall in the months of June and December was recorded as 151 and 6.8 mm respectively.

146

147 **2.2 Sampling**

148 Collocated Minivol samplers (AirMetrics, Springfield, OR) equipped with PM_{2.5} impactors were
149 used to collect two twelve hour PM_{2.5} samples per day (filter change at 12:00 and 00:00 ; n=28 in
150 summer, n= 15 in winter) on 47 mm quartz fibre (Tissuquartz 2500QAT-UP, Pall Life Sciences
151 (7202) (Ann Arbor, MI)) and PTFE teflon membrane (Telfo[®] PTFE membrane with PMP
152 (polymethpropylene) support ring, 2µm pore size, Pall Life Science (R2PJ047) (Ann Arbor, MI))
153 filters. Use of a low volume sampler with a flow rate of 5L/min was more suitable in Delhi to
154 minimize clogging since the area records high PM concentrations. Teflon-membrane filters were
155 equilibrated in a temperature (21-23 °C) and RH (30-40%) controlled room before gravimetric
156 analysis. Pre- and post-weighing of filters was performed with a microbalance (Mettler (Toledo,
157 OH) Model XP-6) with a sensitivity of ± 1µg. Quartz fibre filters were baked at 900 °C for four
158 hours to remove organic artefacts. All samples were analysed at the Environmental Analysis
159 Facility, Desert Research Institute (Reno, Nevada, USA).

160

161 **2.3 Chemical Analysis**

162 The PTFE filter samples were analysed for elements from Na to U at DRI using energy dispersive
163 X-ray fluorescence (ED-XRF) (PANalytical Epsilon 5) and calibration was performed using
164 MicroMatter thin-film standards (Watson et al., 1999) while sulphate (SO₄²⁻), nitrate (NO₃⁻),
165 chloride (Cl⁻), ammonium (NH₄⁺), sodium (Na⁺) and potassium (K⁺) and carbohydrates (mono- and
166 disaccharides and anhydrosaccharides) were analysed using Ion Chromatography (Thermo Dionex
167 (Sunnyvale, CA) Model ICS 3000 for anions and carbohydrates and Model ICS 2100 for organic
168 acids) (Chow and Watson, 1999). The samples were also analysed for straight chain alkanes,
169 polycyclic aromatic hydrocarbons (PAHs), hopanes and steranes (details in SI) using Thermal
170 Desorption-Gas Chromatography-Mass Spectrometry (Agilent (Santa Clara, CA) Model
171 6890/5975C TD-GC-MS) with an HP-5MS capillary column in SCAN mode (Ho and Yu, 2004;

172 Chow et al., 2007a). Internal standards used in the analysis include $nC_{16}D_{34}$ and $nC_{24}D_{50}$ for alkanes
173 and phenanthrene- d_{10} and chrysene- d_{12} for PAHs. Experimental details of the method for hopane
174 and sterane analysis are reported by Ho et al. (2008). The samples were also analysed for carbon
175 fractions (OC1, OC2, OC3, OC4, OP, EC1, EC2 and EC3) using the DRI Model 2001
176 Thermal/Optical Carbon analyser (DRI (Reno, NV) Model 2001) following the IMPROVE_A
177 thermal/optical reflectance protocol (Chow et al., 2007b). Organic carbon (OC) is defined as the
178 sum of OC1-4 and pyrolyzed carbon (OP), and elemental carbon (EC) is defined as the sum of EC1-
179 3 minus any OP.

180

181 **2.4 Data Analysis**

182 Data analysis has been carried out using Microsoft Excel and SPSS (Version 21). Several species
183 were detected in less than 20% of the samples and are not included in further analysis.
184 Concentrations below detection limits were replaced with $0.5 \times$ detection limit. Correlation analysis
185 of analyte concentrations was conducted using SPSS based on Pearson Correlation and the
186 correlation values reported in the text are for $p < 0.01$. Reduced major axis (RMA) regression
187 analysis has been used in most cases due to similar uncertainties of the different species.

188

189 **3. RESULTS**

190 **3.1 Particulate Matter**

191 The average 12h concentration in summer was observed to be $58.2 \pm 35.0 \mu g/m^3$ with a maximum
192 $PM_{2.5}$ concentration of $179.5 \mu g/m^3$ while in winter; the average concentration was 276.9 ± 99.9
193 $\mu g/m^3$ with a maximum of $424.9 \mu g/m^3$ (details in Table 1). Several studies have reported ambient
194 $PM_{2.5}$ concentrations in New Delhi, and most of them report concentrations in exceedance of the
195 Indian $PM_{2.5}$ NAAQS of $60 \mu g/m^3$ irrespective of site type (Singh et al., 2011; Tiwari et al., 2014;
196 Trivedi et al., 2014). Additionally, studies in other Indian cities, including Chennai have reported
197 higher concentrations in the winter season (Srimuruganandam and Shiva Nagendra, 2012). A

summary of relevant studies is presented in Table S1. Continuously monitored PM_{2.5} data for New Delhi are not in the public domain, but these data help to put the concentrations measured during our campaign into context. The summer mean in our study was slightly lower than in most other studies while the winter mean was slightly higher (Table S1). However the broad conclusion is that our site well represented PM_{2.5} concentrations typical of Delhi.

Concentrations in winter were consistently higher compared to summer and this can be due to the differences in meteorological parameters as well as variations in source strengths. Significant differences between PM concentrations in summer and winter have been recorded previously (Guttikunda and Gurjar, 2012; Yadav et al., 2013; Tiwari et al., 2014), and higher winter concentrations are attributed to larger combustion source strength in the winter combined with calm weather conditions and a shallow boundary layer which affects pollutant dispersion adversely.

If the 12-h concentrations are compared (i.e. 00:00-11:59 AM and 12:01- 23:59 PM), the concentrations are ~ 1.2 times higher for the 00:00-11:59 AM period in both seasons (Figure 2). This is expected since this period corresponds with HDV movement across the city at night, and includes the morning traffic peak. EC was found to be higher for the 00:00-11:59 AM period while the OC concentrations were higher during the 12:01- 23:59 PM. EC is typically associated with traffic emissions, and the concentrations are expected to be higher when the volume of heavy duty vehicle traffic increases. On the other hand, OC can be contributed by primary as well as secondary sources, and concentrations are likely higher during the day when combustion activities (e.g. cooking, waste burning), as well as photochemical reactions (i.e. secondary organic aerosol formation) typically occur.

3.1.1 Carbon

In both summer and winter, the high-temperature OC3 (at 480°C) and OP fractions in helium (He) atmosphere had the highest concentrations among the OC fractions while low-temperature EC (EC1, in 2% O₂/98% He atmosphere) had the highest concentration among the EC fractions. EC3 (at 840°C) was detected in less than 20% of samples in both seasons. This is in line with the previous studies since EC3 is not associated with gasoline or diesel vehicle emissions. A summary is presented in Table 1. Typically, EC2 (at 740°C) and OC1 (at 140°C) are associated with diesel vehicles while EC1, OC2 (at 280°C) and OC3 are dominant in gasoline vehicle emissions (Watson et al., 1994).

OC and EC were found to be reasonably closely correlated both in summer and winter indicating some common sources such as road traffic and biomass burning. Both OC and EC were also correlated well with PM_{2.5} mass in summer although no correlation was observed in winter. Both OC and EC were correlated well with the carbon fractions. If the concentration of OC is expressed as function of concentration of EC using RMA regression, the OC/EC gradient is significant for both seasons (1.19 for summer and 2.15 for winter) (Figure 3). The intercept is greater than 4 µg C/m³ in both cases indicating contributions from other sources of OC unassociated with EC.

EC is emitted directly into the atmosphere and can be used to estimate relative amounts of primary OC (POC) and secondary OC (SOC). Higher OC/EC ratios are expected in the conditions where SOC is dominant and the EC-tracer method involves the use of EC as a tracer for POC, allowing SOC to be calculated (Turpin and Huntzicker, 1995; Castro et al., 1999; Pio et al., 2011). Minimum ratios of OC/EC are taken as representative of primary OC (although they may be an over-estimate) (Pio et al., 2011) and OC above that ratio is taken to be SOC. The method as outlined by Castro et al. (1999) was used and estimates of SOC were calculated (Figure 4).

$$\text{Secondary OC} = \text{Total OC} - \left(\text{EC} \times \left(\frac{\text{OC}}{\text{EC}} \right)_{\text{minimum}} \right) \quad \text{Eq (1)}$$

The minimum ratios were estimated as 0.93 for summer and 1.63 for winter, and were used to calculate the contribution from primary and secondary OC for both seasons. The average contribution of POC was estimated to be 41% in summer and 72.3% in winter while the SOC was estimated to contribute 66.7% in summer, and 33.1% in winter.

3.1.2 Ions

$\text{PM}_{2.5}$ SO_4^{2-} and NH_4^+ were found to be the most abundant ions in summer with average contributions of 17.1% and 8.5% to $\text{PM}_{2.5}$ mass. Higher abundance of SO_4^{2-} in summer and NO_3^- in winter is consistent with previous observations in the region (Satsangi et al., 2013). In winter, NH_4^+ was the most abundant ion followed by NO_3^- contributing 12.4% and 11.8% to $\text{PM}_{2.5}$ mass. A summary of the data is presented in Table 1. NO_3^- and SO_4^{2-} were found to be correlated in summer as well as in winter and high correlation was also observed between SO_4^{2-} and NH_4^+ in summer and winter indicating common sources. SO_4^{2-} and NO_3^- were also moderately correlated with $\text{PM}_{2.5}$ mass in summer but no correlation was observed in winter. Cl^- was not found to be correlated with any of the other ions in summer while in winter, it was correlated with NH_4^+ . Higher concentrations were observed for all ions in winter but Na^+ was present in broadly similar concentrations in both seasons with a winter/summer ratio of less than 2. On the other hand, Cl^- , NO_3^- and NH_4^+ showed the highest winter/summer ratios. It is worth noting that particulate nitrate when present as NH_4NO_3 is semi-volatile (Allen et al., 1989), and at higher temperatures NO_3^- is volatilized from the particle phase. Seasonal variations in concentrations of ions have also been reported by Sudheer et al. (2014), and Tiwari et al. (2013) reported higher chloride concentrations in Delhi during winter.

273 Cl^- and NO_3^- (or their precursors HCl and NO_x) have been reported to be emitted during wood
 274 combustion and K^+ is widely used as a marker for biomass combustion (Kleeman et al., 1999;
 275 Simoneit et al., 2004; Watson et al., 2008). In India, Patil et al. (2013) reported a high abundance of
 276 Cl^- and K^+ in wood combustion, open burning and coal combustion while NH_4^+ , NO_3^- and Cl^- are
 277 reported to be abundant in industrial emissions. The high winter concentration of Cl^- could be due
 278 to the increased burning (wood, coal, waste) in the winter season, but like ammonium nitrate,
 279 ammonium chloride is semi-volatile (Pio and Harrison, 1987a,b) causing loss to the vapour phase
 280 during conditions of higher temperature and lower relative humidity in summer.

281
 282 Ion equivalency was estimated using Cl^- , SO_4^{2-} , NO_3^- (anions) and NH_4^+ (cation) for both seasons to
 283 understand the neutralization of the ions in the atmosphere (Figure 5) and the anions were found to
 284 be more or less neutralized by NH_4^+ in both seasons.

285 3.1.3 Elements

286
 287
 288 S, Si, and Al were found to be the most abundant elements in summer and winter (Table 1).
 289 Concentrations of several elements including Cl, Pb, Fe and Zn were found to be more than five
 290 times higher in winter compared to summer. Elements typically associated with soil/mineral dust
 291 showed the lowest winter/summer ratios (e.g. Si- 0.95; Ca- 0.80) while several other species
 292 showed a 1.5 to 4 times increase in concentrations in winter (e.g.- Cr- 1.41; Mn- 2.69; S- 3.14; Zn-
 293 3.27; Cu- 4.74).

294
 295 Correlation analysis was used to identify associations among different elements. Zn was found to be
 296 moderately correlated with Pb and Br in summer, while a strong correlation was observed in winter
 297 for Pb. Previous studies have also reported correlation between Zn and Pb and Tiwari et al. (2013)
 298 used these as markers for traffic source and Chen et al. (2011) reported association of Fe, Zn, Pb

and Br with diesel vehicles. Pb and K⁺ have also been used as markers for biomass burning (Cheng et al., 2013) but no correlation was observed between these two species in Delhi.

Al, Si, Ca, Ti, Mn and Fe have been used as markers for crustal dust/soil (Cass, 1998; Chow et al., 2004; Viana et al., 2008; Pant and Harrison, 2012; Tiwari et al., 2013). In summer, Si was strongly correlated with Al, Fe, Ca, Ti, Sr and moderately correlated with Mn and K and weakly correlated with Ni. In winter, Si was strongly correlated with Fe, Ca, Ti but Al was not found to be correlated with the other soil-associated elements but with Cl, Br and moderately correlated with Cu, Zn, and K. This is probably due to anthropogenic sources of Al, particularly from metallurgical industries, coal burning and traffic.

In addition to its correlation with Zn, Pb was correlated with As, K and moderately correlated with S and Na. In summer, Pb was moderately correlated with S, Br, Zn, Cu and V. As was also correlated with Zn in winter though these elements were not found to be correlated in summer. As and Pb are also reported to be emitted from waste burning (Watson et al., 2008). V and Ni are associated with industrial emissions as well as oil combustion (Viana et al., 2008). Pb, Fe, Zn and K have also been associated with industrial emissions (Sahu et al., 2011b; Moreno et al., 2013; Patil et al., 2013; Farao et al., 2014). K and Br have also been reported from wood smoke (Kleeman et al., 1999; Fine et al., 2001) while Zn has been associated with incineration (Harrison et al., 1997; Moreno et al., 2013) and industrial burning (Duvall et al., 2012). Pb and Mg are also reported to be emitted from kerosene combustion (Patil et al., 2013). While the correlations in the summer season are largely indicative of traffic and industrial sources, an additional source, most likely, combustion (including biomass, coal and waste) is affecting elemental concentrations in the winter season. Zn and Cl can both be emitted from coal combustion, and waste incineration (Perrino et al., 2011). In

winter, brick kilns are also reported to operate in areas surrounding Delhi, and can contribute to PM concentrations observed in the city (Guttikunda and Calori, 2013).

Elements such as Cu, Ba, Sb and Sn have been associated with brake wear (Pant and Harrison, 2013) but in Delhi, these were not found to be correlated with each other in summer. Species associated with brake wear such as Cu and Ba typically exhibit a coarse mode peak at 3.2-5.6 μm (Gietl et al., 2010). However, in Delhi, these peaks were not observed (unpublished data). This is important for future studies, as this would imply that elements such as Cu and Ba cannot readily be used as markers for non-exhaust emissions in India, and further research is required to characterize appropriate markers for non-exhaust emissions.

3.1.4 Hopanes and steranes

Total hopane concentration was observed to be $1.97 \pm 2.47 \text{ ng/m}^3$ in summer and $26.3 \pm 7.93 \text{ ng/m}^3$ in winter. C31 $\alpha\beta$ R-hopane was the most abundant species in both seasons (Table 1, SI). Hopanes were found to be strongly correlated to alkanes and PAHs in winter although no correlation was observed with OC and EC. In summer, hopanes were strongly correlated with EC and PAHs and moderately correlated with OC and alkanes, indicating a traffic source. While hopanes are typically used as markers for traffic exhaust emissions (Lin et al., 2010; Pant and Harrison, 2013), several hopane species are also found to be abundant in coal burning emissions (Oros and Simoneit, 2000; Zhang et al., 2008). The ratio between S/S+R homohopane isomers was identified as 0.05 for lignite and 0.08 for brown coal (Oros and Simoneit, 2000). In Delhi, the values for this ratio were calculated as 0.11 for summer and 0.05 for winter, indicating the potential contribution from coal/lignite burning as an additional hopane source. Lignite is used for electricity generation in thermal power plants in India, and coal can also be used for cooking and/or heating, particularly in poorer areas and slums.

In the case of steranes, $\alpha\beta\beta$ 20R-Cholestane was the abundant sterane in summer while $\alpha\beta\beta$ 20S 24R-Ethylcholestane was the most abundant species in winter. Total sterane concentrations in summer and winter were 0.44 ± 1.04 and 3.95 ± 1.49 ng/m³ respectively. $\alpha\beta\beta$ 20S 24S-Methylcholestane showed a very high winter/summer ratio (15.2) while $\alpha\alpha\alpha$ 20R-Cholestane and $\alpha\alpha\alpha$ 20R 24R-Ethylcholestane showed winter/summer ratios less than 2. Steranes were strongly correlated with hopanes and EC in summer and in winter, the correlation was moderate both in the case of hopanes and steranes at $p<0.05$.

3.1.5 Alkanes

Alkanes were the most abundant class among the organic species and the 12-h average alkane concentration was observed to be 48.1 ± 38.9 ng/m³ in summer and 382 ± 137 ng/m³ in winter. C20-31 homologues were the most abundant while C39 and C40 were not detected in either season. Fu et al. (2010) also did not detect C36-40 homologues in winter and C39-40 in summer in Chennai (India). The dominant homologues were C26, C27 and C25 in summer and C29, C22 and C31 in winter. Dominance of C29 and C31 homologues in winter indicates contribution from vegetative emissions, possibly through burning of biomass. The winter/summer ratios were highest for the lower homologues (C18-C23) and C34-35, probably reflecting greater partitioning into the condensed phase in the cooler months.

Wood and biomass combustion is quite common in Delhi during the winter period when they are used not only as a cooking fuel but also for heating (Fu et al., 2010; Yadav et al., 2013). In addition, tyres, old furniture and waste materials are often burnt in the open. Long chain alkanes (e.g. C36) are also reported to be emitted from open waste burning (Fu et al., 2010; Alves et al., 2012). Alkane emissions ($n<25$) from the vehicles can be attributed to unburnt engine oil in the case of gasoline vehicles and fuel as well as lubricating oil in case of diesel vehicles, and older vehicles are often high emitters of n-alkanes (Rogge et al., 1993).

374

375 Alkanes were found to be correlated well with OC, and hopanes and moderately correlated with
376 PAHs and EC) in summer. In winter, however, no correlation was observed with OC and EC
377 although strong correlation was observed with hopanes as well as PAHs ().

378

379 Carbon Preference Index (CPI), the ratio of odd to even numbered homologues, can be used to
380 estimate the relative contribution of anthropogenic and biogenic sources. Due to the odd carbon
381 number preference in case of vegetative material, higher ratio values are associated with a biogenic
382 contribution. In this case, the index value was 1.09 for summer and 1.22 for winter indicating a
383 significant contribution from anthropogenic sources in both seasons.

384

385 3.1.6 PAHs

386 PAHs are typically emitted as a by-product of combustion (including road traffic, solid fuel
387 combustion, coal combustion, industries and agricultural burning) and are found both in gas- and
388 particulate-phases (Smith and Harrison, 1996; Cass, 1998; Chow et al., 2004). The total particulate
389 (pPAH) concentration was observed to be $7.73 \pm 5.54 \text{ ng/m}^3$ in summer and $119 \pm 33.8 \text{ ng/m}^3$ in
390 winter. Several species including picene (Pic), dibenzo(a,e)pyrene (DaeP), coronene (Cor) were
391 detected only in winter samples. Acenaphthylene (Acy) was the most abundant species in summer
392 followed by acenaphthene (Ace), while in winter chrysene (Chr) was the most abundant species
393 followed by benzo(a)pyrene (BaP). PAHs were strongly correlated with OC, EC and hopanes in
394 summer and moderately correlated with alkanes suggesting a traffic source.

395

396 HDVs typically emit low molecular weight PAHs including anthracene (Ant), methyl- and
397 dimethyl-phenanthrenes and fluoren-9-one (Rogge et al., 1993; Sjorgen et al., 1996; Miguel et al.,

1998). Species such as benzo(b)naphtho(1,2-d)thiophene (BN1NT), fluorene (Flu), phenanthrene (Phe) have been used as markers for diesel vehicle emissions while methylphenanthrenes have been associated with evaporative emissions from fuel (Harrison et al., 1996; Jang et al., 2013). PAHs such as benzo(ghi)perylene (BghiPe), indeno(1,2,3-cd)pyrene (IcdP) and Cor have previously been used as markers for gasoline traffic emissions (Cass, 1998; Phuleria et al., 2007; Pant and Harrison, 2013). Flu, Acy, Ant, Phe, Pyr, benzo(e)pyrene (BeP), BaP, retene (Ret) are typically used as markers for wood combustion (Cass, 1998; Fine et al., 2001; Simoneit, 2002; Jang et al., 2013) while Ant, Phe, benzo(a)anthracene (BaA) and Chr are used as markers for coal combustion (Harrison et al., 1996). Several species such as Ant, cyclopenta(cd)pyrene (CcdP) and BN1NT have been attributed to various sources in different studies. For example, Larsen and Baker (2003) reported the use of CcdP as a tracer for gasoline emissions while Jang et al. (2013) used it as a marker for coal combustion. Previous studies from India have associated pyrene with domestic fuel emissions (kerosene, dung etc.) and coal combustion, BaP with wood combustion and BghiPe and IcdP with traffic emissions (Kulkarni and Venkataraman, 2000; Sharma et al., 2007) while benz(a)anthracene-7,12-dione (BaAQ) has been associated with residential natural gas emissions (Cass, 1998).

If the summer and winter concentrations are compared, species such as Phe (11.6) and BaA (54.7) associated with coal and biomass combustion show very high winter/summer ratios while others associated with traffic such as BghiPe (6.86) and 2-Methyl phenanthrene (2MPhe) (2.50) have comparatively lower winter/summer ratios. This indicates additional sources in the proximity of the sampling site during the winter season which is consistent with emission inventory analyses. High winter/summer ratios have been reported previously by Sharma et al. (2007) for Delhi. In addition to source types, the different temperature regimes across seasons can also influence the partitioning of the species in the gas- and particle- phases for PAHs (Smith and Harrison, 1996).

One of the qualitative approaches for assessment of PAH source is diagnostic ratio (DR) analysis where ratios of different PAHs are used for identification of contributing sources. The ratio of IcdP/IcdP+BghiPe is used as an indicator for diesel/gasoline or coal emissions (Ravindra et al., 2008). The ratio was observed to be 0.38 in summer and 0.46 in winter indicating a contribution from vehicular emissions. The ratio of BaA/BaA+Chr can also be used to distinguish between diesel/gasoline/wood combustion and in the present case, the ratio was observed to be 0.18 for summer and 0.39 for winter which corresponds with diesel emissions (Kavouras et al., 2001). HDVs are reported to emit higher concentrations of lighter PAHs such as Pyr, BaA and Chr compared to heavier PAHs such as BghiPe and coronene (Miguel et al., 1998). The site gets a high volume of interstate HDV traffic, and often the trucks are run on high sulphur fuel.

3.1.7 Sugars

In ambient air, saccharides are typically associated with biological material (e.g. soil organic matter) and arabitol and mannitol have been proposed as markers for fungal spores (Simoneit et al., 2004; Buaer et al., 2008). Glycerol was the only saccharide species detected in both summer and winter with a winter/summer ratio of 26.5. Most of the other saccharides were detected in less than 20% of the samples and are not discussed in detail (Table 1).

Anhydrosaccharides such as levoglucosan and mannosan are typically associated with wood/biomass combustion (Simoneit et al., 2004; Alves et al., 2012). Both levoglucosan and mannosan were only detected in the winter season and had a strong correlation. Levoglucosan was also strongly correlated with OC and Cl⁻. Correlation with K⁺ was comparatively weaker, and not significant at p<0.01. Fu et al. (2010) reported a levoglucosan/mannosan ratio of 16.4 which is comparable to the ratio observed in the current study (16.07). Cow dung burning has also been

identified as a source of levoglucosan in India, but K is typically not released from cow dung combustion (Fu et al., 2010). A recent study focused on water soluble organic carbon (WSOC) has also highlighted the importance of biomass combustion as a source of OC in Delhi (Kirillova et al., 2014).

3.1.8 Diacids

Several organic acids including oxalic acid, lactic acid and glutaric acid were found to be present in both seasons. While oxalic acid was found to be the abundant species in both seasons, formic acid had the highest winter/summer ratio of 3.14. Biogenic sources have been reported to contribute to malic acid precursors, and the absence of the compound in this sample set is consistent with the absence or low concentrations of other biogenic material-related molecular markers.

3.2 Enrichment Factors

In order to further understand the sources of the elements (crustal vs. anthropogenic), enrichment factors (EFs) were calculated based on continental crust concentrations using Al as the reference element (Taylor and McLennan, 1995) (selected species are presented in Figure 6).

$$\text{Enrichment Factor (X)} = \frac{\left\{ \frac{\text{Concentration(X)}}{\text{Concentration(Reference)}} \right\}_{\text{sample}}}{\left\{ \frac{\text{Concentration(X)}}{\text{Concentration(Reference)}} \right\}_{\text{crustal}}} \quad \text{Eq (2)}$$

EF values of 10 or higher are considered to indicate significant anthropogenic contribution. High enrichment factors were observed for elements such as Ti, Cu, Zn, Sb, Cd, Sn, As and Pb both in summer and winter, with higher enrichment observed in winter. Ti, typically associated with crustal matter, was also found to be enriched in both seasons although contrary to other elements, the enrichment was higher in summer. Similarly, EFs for Sb and Sn were higher for the summer

471 compared to winter. EF for As was found to be several fold higher in winter (~36 times) compared
472 to the summer. Cr showed similar enrichment in summer and winter seasons. Cd is primarily
473 emitted from industries (smelting), waste incineration and recycling of electronic waste but is also
474 associated with traffic emissions (Amato et al., 2011b). As is used as a marker for coal combustion,
475 and Pb and Zn are also emitted from waste incineration. On the other hand, elements such as Si, Fe,
476 Ca, Ba, Mn, Mg, Sr and Se were present in concentrations similar to the upper continental crust
477 (Taylor and McLennan, 1995).

479 3.3 Mass Closure

480 In order to understand the relative contribution of the different species, mass closure was attempted
481 for PM_{2.5} mass with seven key components including woodsmoke, traffic, other OM, secondary
482 aerosol (ammonium chloride, ammonium nitrate and ammonium sulphate) and mineral dust/soil
483 (Table 2). A little over 100% of the measured mass was accounted for in both cases (115.4% in
484 summer and 114.2% in winter) and the results are described in Figure 7.

486 Crustal material was estimated using concentrations of elements- Si, Al, Ca, Fe and Ti, based on
487 Chan et al. (1997). Organic matter (OM) was estimated from OC using a factor of 1.2 in the case of
488 traffic OM, and 1.5 in the case of other OM, which was considered as largely secondary.

490 OM was found to be the highest contributor to mass in summer (33.3%) while woodsmoke was the
491 primary contributor to PM_{2.5} mass in winter (23.3%) (details in Figure 6). Ammonium sulphate
492 (20.5 %) and crustal material (14.3%) had higher contributions in summer while ammonium nitrate
493 (12.4%) had a higher contribution in winter. A lower concentration of nitrate in summer can be
494 explained by the volatility at higher temperatures while higher crustal matter in summer (14.3%) is
495 attributed to desert dust as well as local dust sources which are frequently resuspended in dry and

windy conditions. Traffic was found to contribute 18.7% in summer and 16.2% in winter, while woodsmoke was found to contribute 23.3% in winter.

Table 3 summarizes results from source apportionment studies conducted in New Delhi. While most studies report traffic, road dust, coal combustion and biomass as key sources of PM in New Delhi, there is a large variability in the quantitative estimation of source contributions. Some of the variability is introduced by the differences in the computational methods. For instance, while most receptor models use the principle of mass conservation; the CMB model takes into consideration the chemical profiles of individual sources, while the mass closure approach relies on individual tracers. In addition, most of the studies conducted in Delhi have analysed inorganic species (elements and ions) and recent studies have included carbon (OC/EC). In addition, choice of sampling location can often drive differences in the results, especially when site types have significantly different characteristics. In a CMB study in New Delhi, Chowdhury et al. (2007) identified five major sources including road dust, coal combustion, diesel and gasoline exhaust and biomass combustion at an urban residential site. These are in line with the source inferences drawn in this study, and while the quantitative contributions are a little different between the 2007 study and the current study, overall trends with a high contribution from road dust in summer, and biomass combustion in winter are similar. It is important to remember that the site characteristics are not comparable between the two sites, and differences in local source strengths can introduce differences in the overall source contribution estimate. The contribution of secondary aerosol was not estimated in their study. For comparison, a study in 2012 in Mumbai found the contribution of secondary inorganic aerosol to be 23% of total $PM_{2.5}$ mass while crustal material was reported to contribute 11% of $PM_{2.5}$ mass, and in Chennai, the contribution of secondary aerosol was estimated as 42% of $PM_{2.5}$ mass (Joseph et al., 2012).

It is important to note that some of the factors used in the current mass closure calculation are derived from the literature and may not be directly representative of the Indian situation. For example, the woodsmoke estimation factors utilized in this study are based on measurements made in Europe, and due to differences in the wood type, and the burning conditions, the ratios may not accurately represent the contribution of woodsmoke in an Indian city. Also, this can introduce uncertainty in the overall estimation. As a next step, locally developed source profiles (Patil et al., 2013; Matawle et al., 2014) will be tested for a CMB model.

4. CONCLUSIONS

PM_{2.5} samples were analysed for a heavy traffic site in New Delhi, and detailed chemical characterization was conducted including analyses of metals, ions, carbon and molecular markers. PM concentrations were found to be higher than the 24-hour PM_{2.5} NAAQS ($60 \mu\text{g}/\text{m}^3$) on several occasions in summer and on all days in winter. Several elements including Cu, Zn, Pb, Cd and As were found to be significantly enriched and complex correlations were observed between elemental species. In the case of molecular markers, several combustion-related species were detected only in winter. Alkanes were found to be the most abundant class of organic species followed by PAHs and hopanes.

Concentrations were found to be significantly higher in winter compared to summer. Pollutant concentrations can be affected both by meteorology and source strength. There is an appreciable difference in the average temperature between summer and winter seasons in Delhi, and this could be driving some of the differences between species' concentrations in the two seasons. At higher temperatures, several species can be easily volatilized and reactive species can often undergo chemical reactions in presence of sunlight (e.g. photodegradation of PAHs) (Venkataraman and Friedlander, 1994; Smith and Harrison, 1996; Alves et al., 2012). The combination of higher wind

546 speeds and a deeper mixed layer can lead to better dispersion of pollutants in the summer season.
547 However, in winter, there is much less solar radiation, and the weather conditions are often 'calm'
548 in Delhi indicated by zero or very low wind speeds. Further, the inversion layer height is typically
549 much lower in winter. A combination of such meteorological factors can thus contribute to a build-
550 up of pollutants, leading to higher concentrations. Another important aspect is the role of additional
551 sources in the winter season. During the winter season, biomass/waste combustion is often used as a
552 source of heating across the city, a lot of which occurs under uncontrolled conditions in the open
553 areas. An increase in species associated with waste combustion (Pb, Zn, C35 and C36) indicates the
554 potential contribution from this seasonal source at the sampling site. However, in the absence of
555 detailed emission inventories, it is difficult to attribute the elemental concentrations to specific
556 sources. It is also important to characterize the source emissions in detail, in order to separate the
557 contributions from various combustion sources. Lack of enrichment of barium in the samples
558 indicates that the non-exhaust traffic markers typically used in Europe and USA (i.e., Cu, Ba, and
559 Sb) might not be relevant in the Indian scenario.

560

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565

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TABLE LEGENDS

Table 1: Concentration of the main species measured in the summer and winter campaigns.

Table 2: Estimation factors used for mass closure.

Table 3: Summary of receptor modelling studies for New Delhi.

FIGURE LEGENDS

Figure 1: Modal split at the sampling location in Delhi.

Figure 2: Relationship between OC and EC in summer and winter.

Figure 3: Estimation of minimum OC/EC ratio using the EC tracer method.

Figure 4: RMA regression between ammonium and sum (nitrate, sulphate, chloride).

Figure 5: Enrichment factors for select elements.

Figure 6: Mass closure for PM_{2.5} at CRRI.

1014

1015 **Table 1:** Concentrations of the main species measured in the summer and winter campaigns (in
 1016 $\mu\text{g}/\text{m}^3$, organic species in ng/m^3).

Species	Summer				Winter			
	Mean	S.D.	Min	Max	Mean	S.D.	Min	Max
Mass	58.2	35.0	3.30	179.5	276.9	99.9	111.9	424.9
OC	17.6	8.38	5.17	36.4	104.4	40.6	53.3	195.5
EC	7.77	7.06	0.60	31.4	46.3	18.9	12	78.9
<i>Ions</i>								
Chloride	2.14	1.54	0.56	6.70	27.8	18.1	7.21	68.1
Nitrate	4.37	2.14	1.04	8.79	32.8	20.1	0.21	76.7
Sulphate	9.97	6.25	1.74	27.5	26.1	15.3	7.66	59.1
Ammonium	4.94	2.87	0.94	12.4	34.2	17.0	13.0	64.0
Na ⁺	0.41	0.38	0.01	1.56	0.64	0.30	0.20	1.18
K ⁺	0.86	0.49	0.13	2.40	3.83	1.63	1.51	6.50
<i>Anhydrosaccharides</i>								
Levoglucosan	<i>detected in <20% samples</i>				6.57	3.23	2.15	12.0
Mannosan	<i>detected in <20% samples</i>				0.42	0.27	0.06	1.04
<i>Molecular Markers</i>								
Sum of Hopanes (C27-C35)	1.97	2.47	0.00	9.26	26.3	7.93	15.6	40.4
Sum of Steranes (C27-C29)	0.44	1.04	0.00	4.81	3.95	1.49	1.63	6.79
Sum of Alkanes (C14-C40)	48.1	38.9	1.52	145	382	137	168	617
Sum of PAHs (C12-C24)	7.73	5.54	0.82	25.8	119	33.8	84.1	188
Sum of Saccharides (C3-C12)	0.05	0.01	0.03	0.08	1.63	1.77	0.54	7.21
Sum of Diacids (C1-C5)	1.43	0.49	0.65	2.41	3.76	3.12	1.00	9.55
<i>Elements</i>								
Al	0.81	0.72	0.08	3.03	1.73	0.87	0.63	3.74
Si	1.88	1.87	0.02	7.80	1.79	0.67	0.77	2.94
S	3.02	2.20	0.01	9.67	9.49	7.27	2.42	26.9
Ca	0.78	0.75	0.004	3.27	1.11	0.46	0.33	1.85
Cu	0.02	0.01	0.001	0.05	0.07	0.07	0.01	0.28
Zn	0.20	0.19	0.01	0.75	0.64	0.38	0.23	1.47
Mn	0.03	0.03	0.0003	0.11	0.08	0.07	0.01	0.29
Fe	0.71	0.63	0.02	2.52	1.15	0.33	0.53	1.57
Ba	0.03	0.03	0.004	0.13	0.01	0.01	0.01	0.04
Pb	0.08	0.06	0.003	0.27	0.60	0.65	0.08	2.51
Ni	0.004	0.003	0.0003	0.01	0.01	0.01	0.0003	0.02
Ti	0.07	0.06	0.003	0.25	0.07	0.04	0.005	0.13
V	0.01	0.01	0.0004	0.02	0.01	0.01	0.001	0.03
Cr	0.01	0.01	0.0003	0.05	0.01	0.02	0.00	0.06

1017 **Table 2:** Estimation factors used for mass closure.

Source	Component	Estimation factor	Reference
Woodsmoke	Mass	11.2*levoglucosan	Harrison et al. (2012) In summer, since levoglucosan was not detected, this calculation was not included for mass closure.
	OC _w	7.35*levoglucosan	Puxbaum et al. (2007)
	EC _w	0.2*woodsmoke PM _{2.5}	Harrison et al. (2012)
Traffic	EC _t	Total EC- EC _w	In summer, since levoglucosan was not detected, EC mass was not corrected for woodsmoke EC.
	OC _t	0.35* EC _t	Pio et al. 2011
	PM _{2.5}	1.35* EC _t	
	OM (PM _{2.5})	Traffic PM _{2.5} *1.2	Chow et al. (2002)
Other OM		Other OC = Total OC – (OC _t + OC _w) Other OM= Other OC*1.5	Puxbaum et al. (2007), Pio et al. (2011)
Secondary Ions	(NH ₄) ₂ SO ₄	1.38*Sulphate	Harrison et al. (2003) Based on molar ratios
	NH ₄ NO ₃	1.29*Nitrate	
	NH ₄ Cl	1.51*Chloride	
Dust	Crustal Mass	1.16(1.90Al+ 2.15Si+ 1.41Ca+1.67Ti+ 2.09Fe)	Chan et al. (1997)
Total PM	SUM (Woodsmoke, Traffic OM, Other OM, (NH ₄) ₂ SO ₄ , NH ₄ NO ₃ , NH ₄ Cl, Crustal mass)		

1018 EC_t- EC associated with traffic; EC_w- EC associated with woodsmoke, OC_w- OC associated with woodsmoke, OC_t- OC associated with traffic

1019

Table 3: Summary of receptor modelling studies for New Delhi.

Reference	Location	Method	Results (%)
Current study	PM _{2.5} Mathura Road	Pragmatic Mass Closure (elements, ions, OC, EC, molecular markers)	Woodsmoke- 23.3 (w) Traffic- 18.7 (s)/ 16.2 (w) Dust- 14.3 (s)/ 3.9 (w) Sulphate- 20.5 (s)/ 10.6 (w) Nitrate- 8.4 (s)/ 12.4 (w) Chloride- 4.8 (s)/ 12.3 (w) Other OM- 33.3 (s)/ 21.4 (w)
Sharma et al. (2013)	PM ₁₀ CSIR- NPL Campus	PMF (elements, ions, OC and EC)	Soil (20.7) Vehicles (17.0) Secondary-inorganic (21.7) Fossil fuel-coal/heavy oil (17.4) Industry (4.5) Sea salt (4.4)
Li et al. (2014)	TSP (winter) CSIR- NPL Campus	Mass Balance (elements, ions, OC, EC, molecular markers)	Crustal material (48) Organic matter (23) Sulphate (4.9) Nitrate (4.5) Ammonium (2.7) Other (7.2)
Tiwari et al. (2013)	PM ₁₀ IITM Campus (Central Delhi)	PMF/UNMIX (elements, ions)	Road traffic Crustal dust SIA Chloride
Khillare and Sarkar (2012)	PM ₁₀ Residential sites	PCA-MLR (elements)	Crustal (49-65) Vehicular (27-35) Industrial (4-21)
Singh et al. (2011)	PM ₁₀ and PM _{2.5} GGSIP University Campus	Qualitative- diagnostic ratios, enrichment factor (elements, PAHs)	Vehicles, road dust, industries
CPCB (2010)	PM _{2.5} Various sites	CMB (elements, ions, OC and EC)	Vehicles- 7-40 (s)/ Industry- 10-19 (s) Construction- 16-41 (s) Resuspended dust- 17-56 (s)
Tiwari et al. (2009)	PM _{2.5} Two sites in New Delhi		Biomass and fossil fuel burning (80); natural and soil derived particles (~6) [<i>refers to % variance explained</i>]
Srivastava and Jain (2008)	SPM (fine and coarse) Residential	CMB (elements)	Diesel vehicles, industries, paved road dust, gasoline vehicles, solid waste, and soil and crustal dust [<i>in descending order</i>]
Chowdhury et al. (2007)		CMB (elements, ions, OC, EC, molecular markers)	Diesel- 22 (s)/ 10 (w) Gasoline- 2 (s)/ 9 (w) Road Dust- 42 (s)/ 11 (w) Coal- 2 (s)/ 14 (w) Biomass- 7 (s)/ 20 (w) Sulphate- 10 (s)/ 8 (w) Nitrate- 3 (s)/ 7 (w) Ammonium- 3 (s)/ 5(w) Other Mass- 11 (s)/ 17 (w)
Khillare et al. (2004)	SPM Residential/industrial/commercial sites in Delhi	PCA (elements)	Vehicular and industrial emissions (60) Crustal (22) [<i>refers to % variance explained</i>]

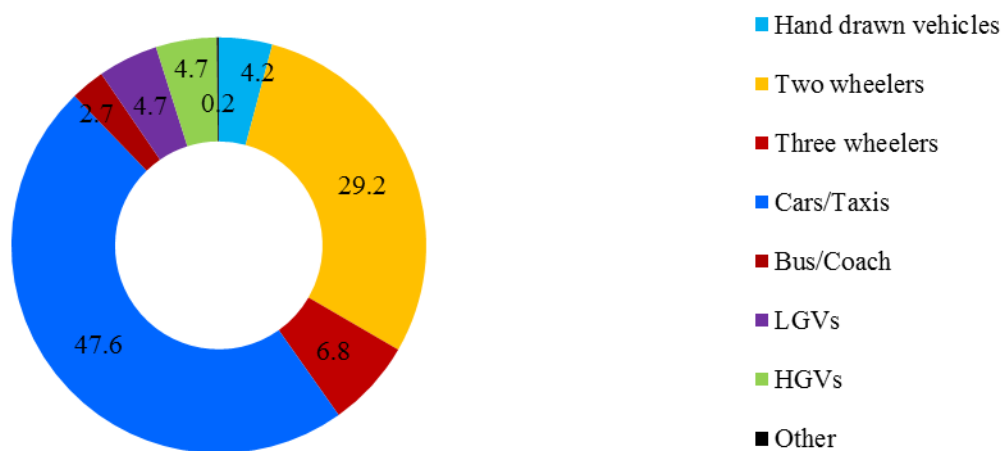


Figure 1: Modal split at the sampling location in Delhi

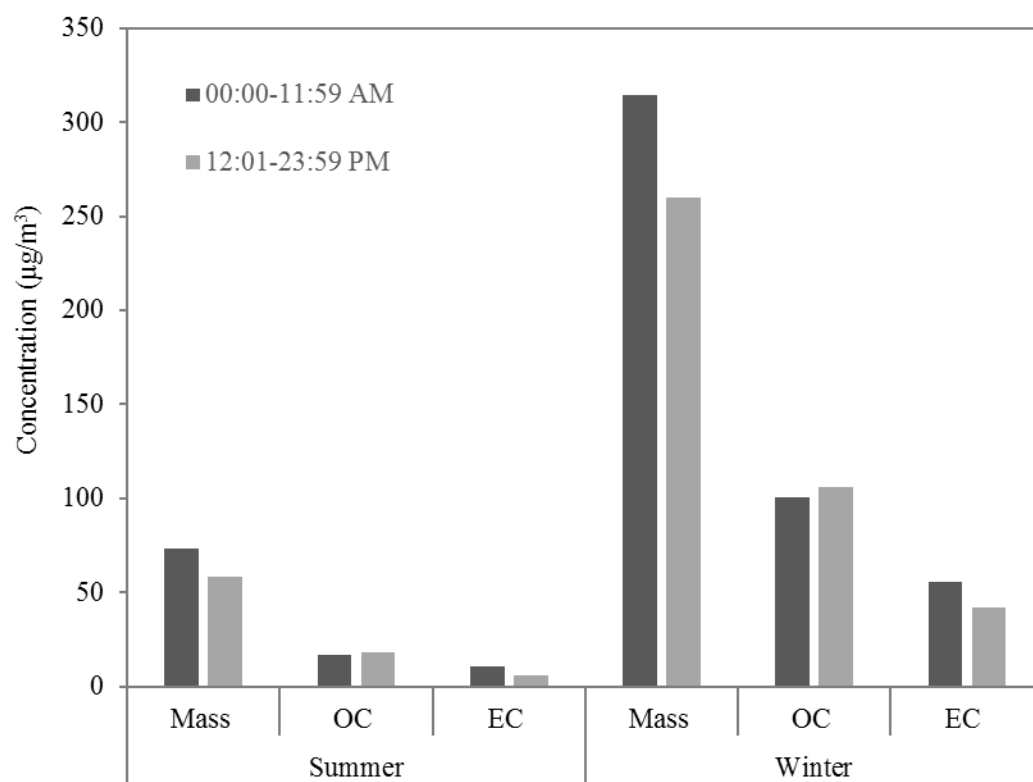


Figure 2: Average 12-h concentrations in summer and winter seasons

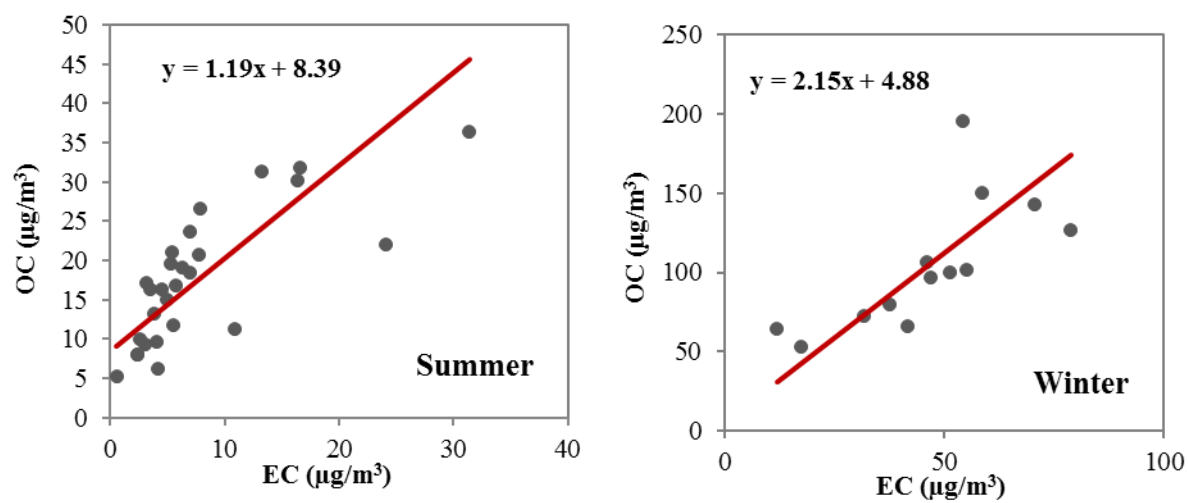


Figure 3: Relationship between OC and EC in summer and winter

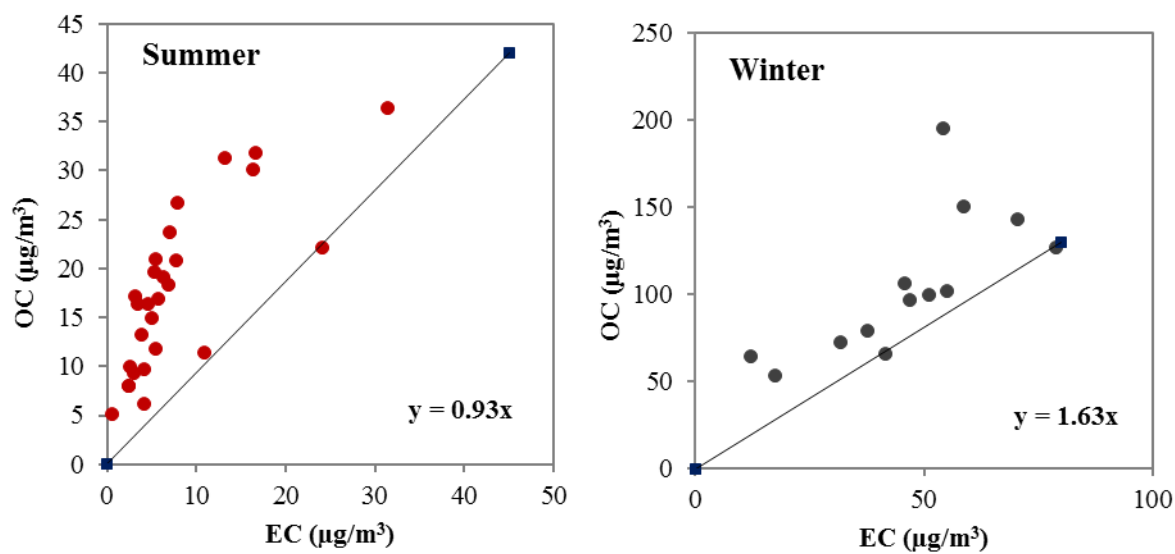


Figure 4: Estimation of minimum OC/EC ratio using the EC tracer method

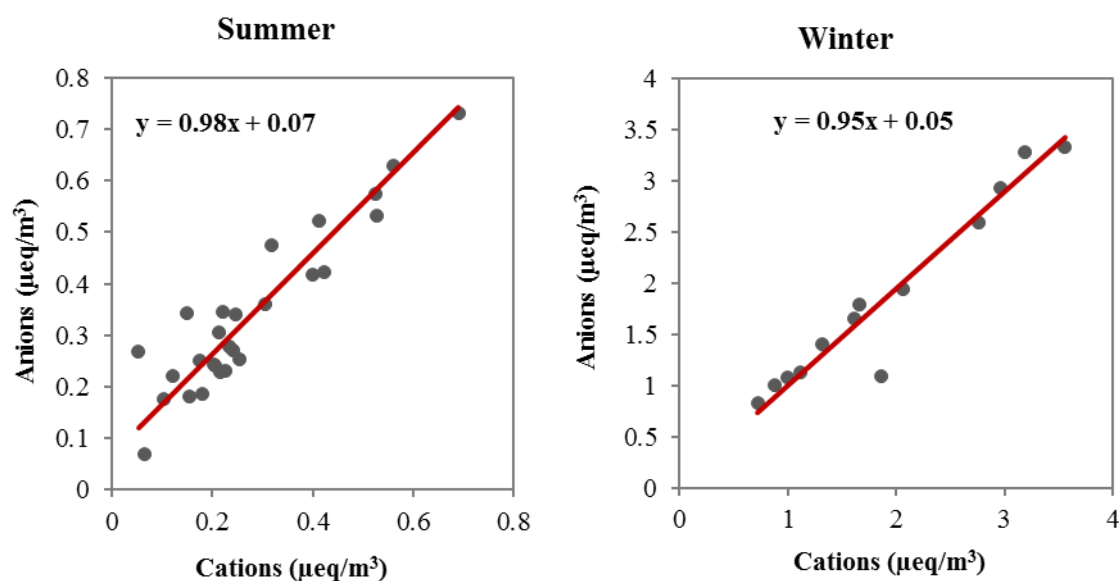


Figure 5: RMA regression between ammonium and sum of anions (i.e. nitrate, sulphate, chloride)

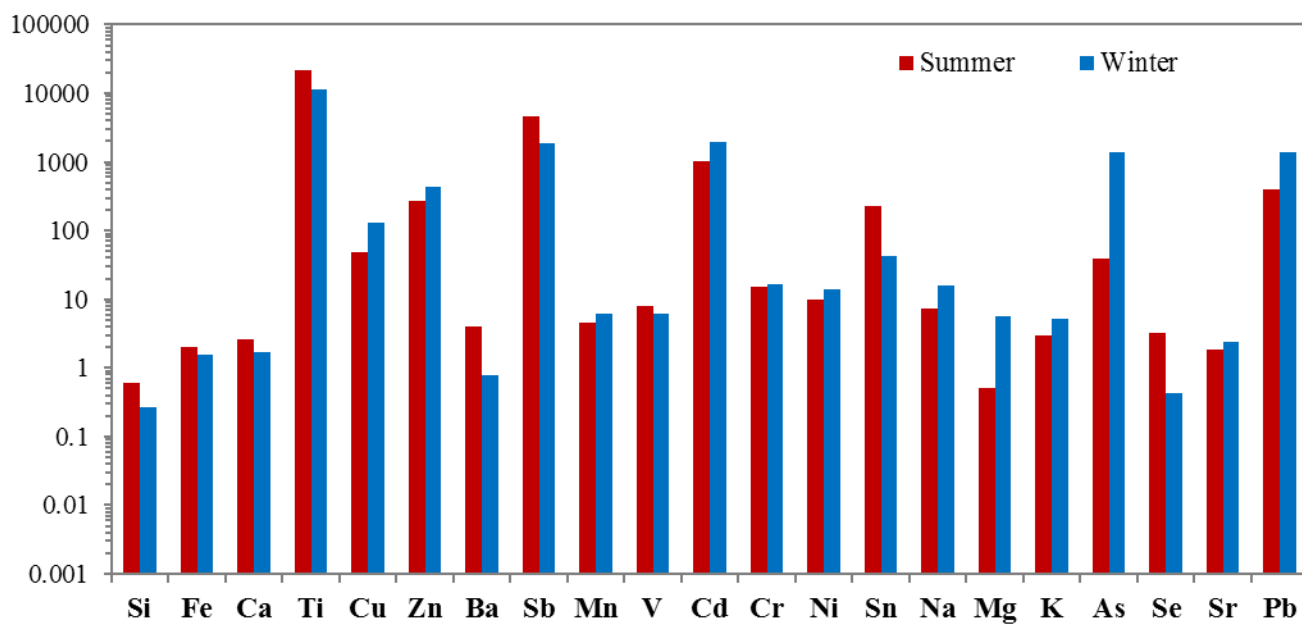


Figure 6: Enrichment factors for select elements

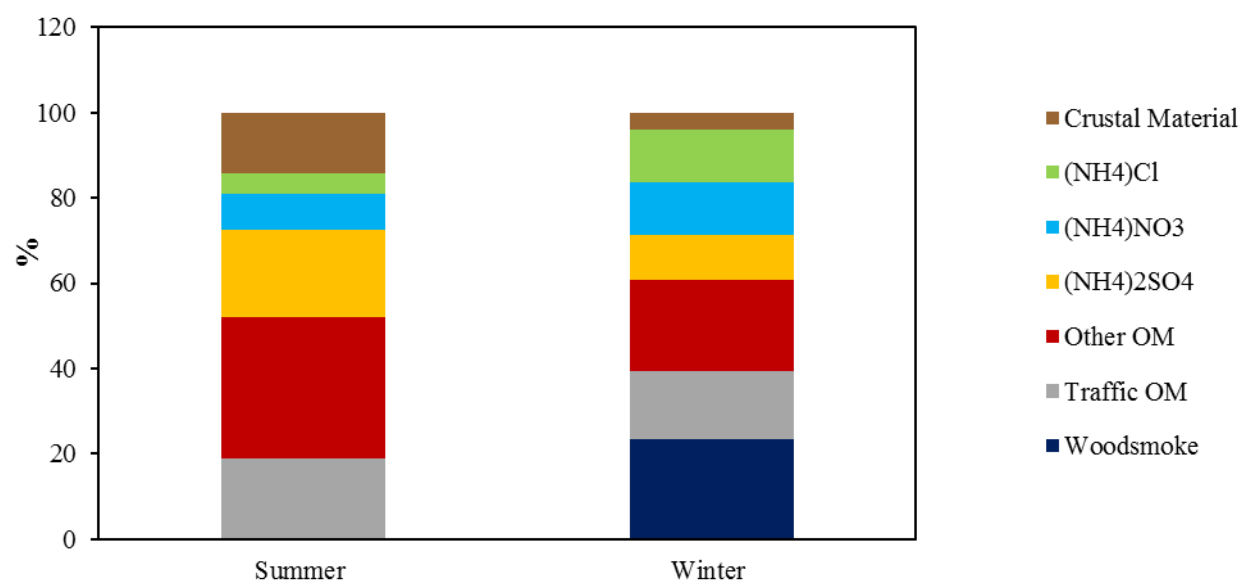


Figure 7: Mass closure for PM_{2.5} at CRRI

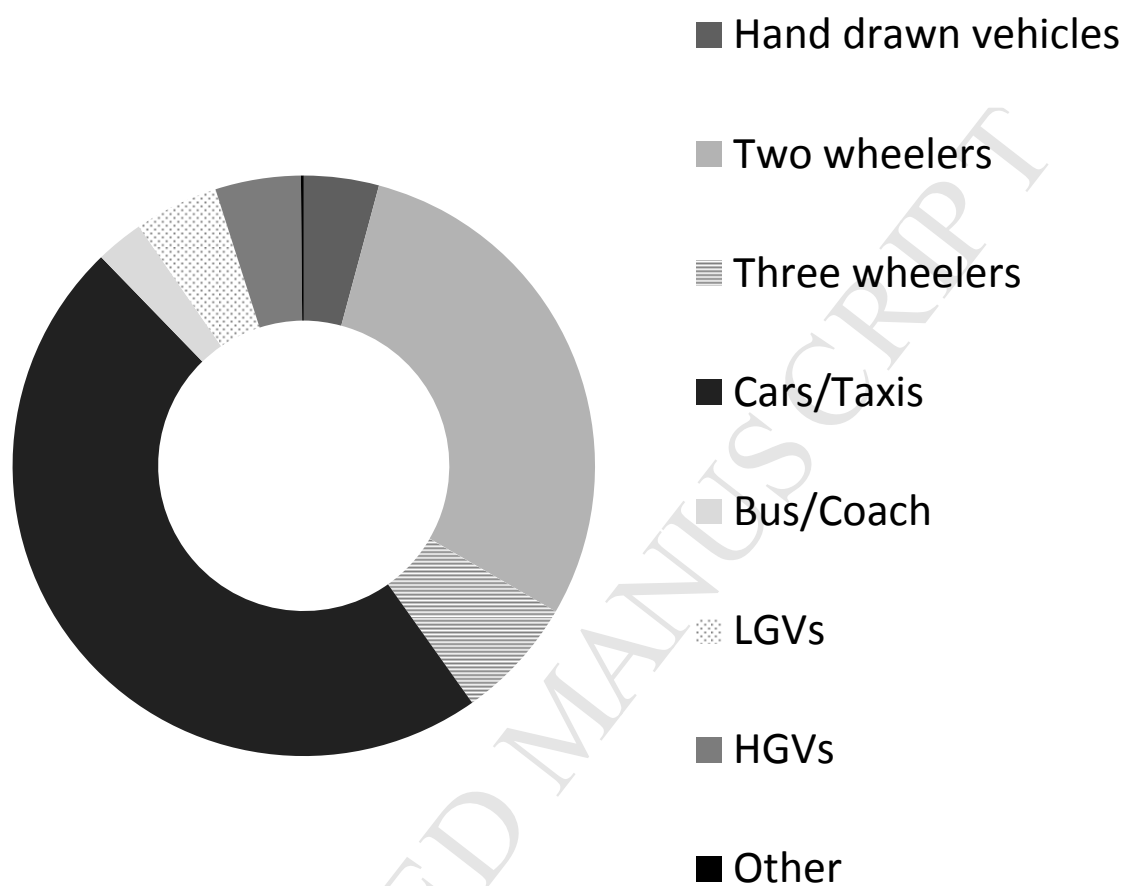


Figure 1: Modal split at the sampling location in Delhi

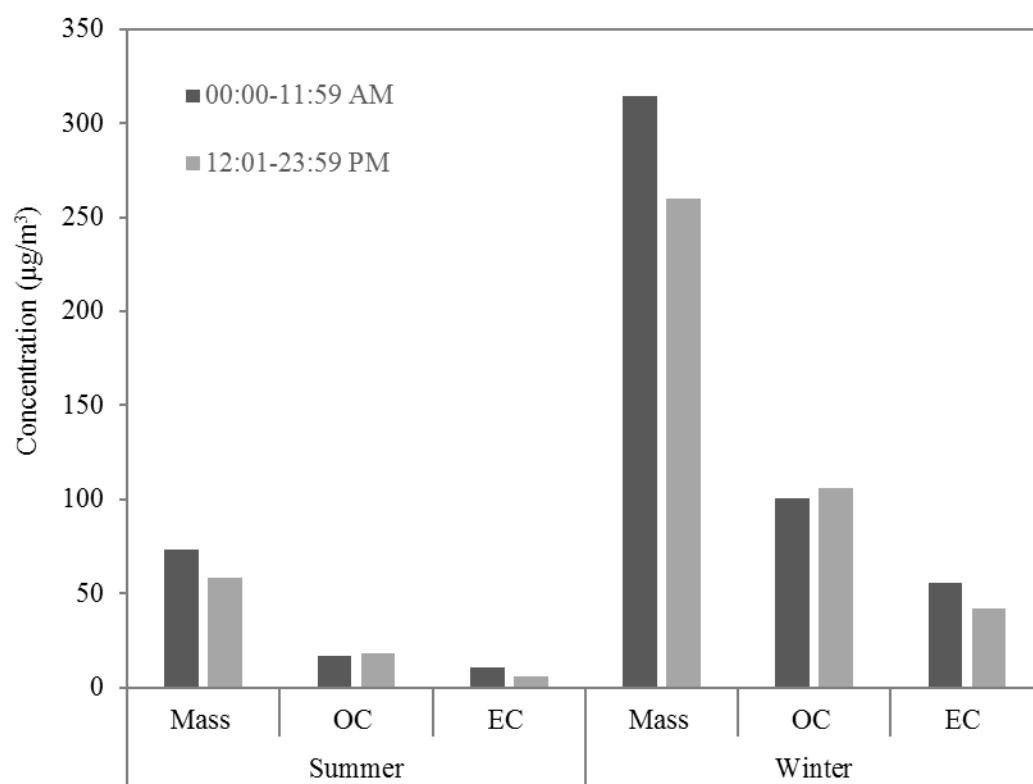


Figure 2: Average 12-h concentrations in summer and winter seasons

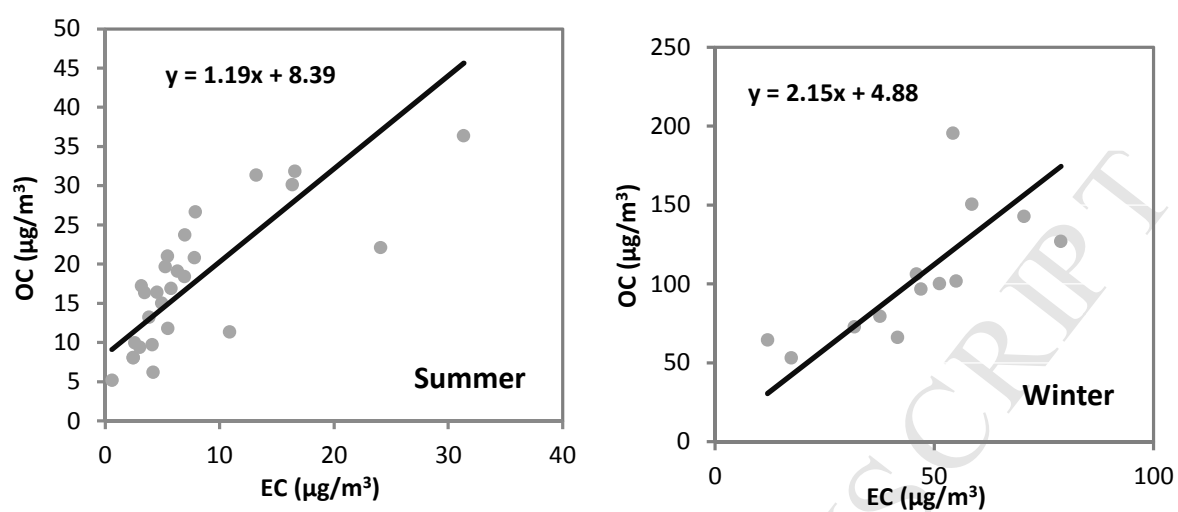


Figure 3: Relationship between OC and EC in summer and winter

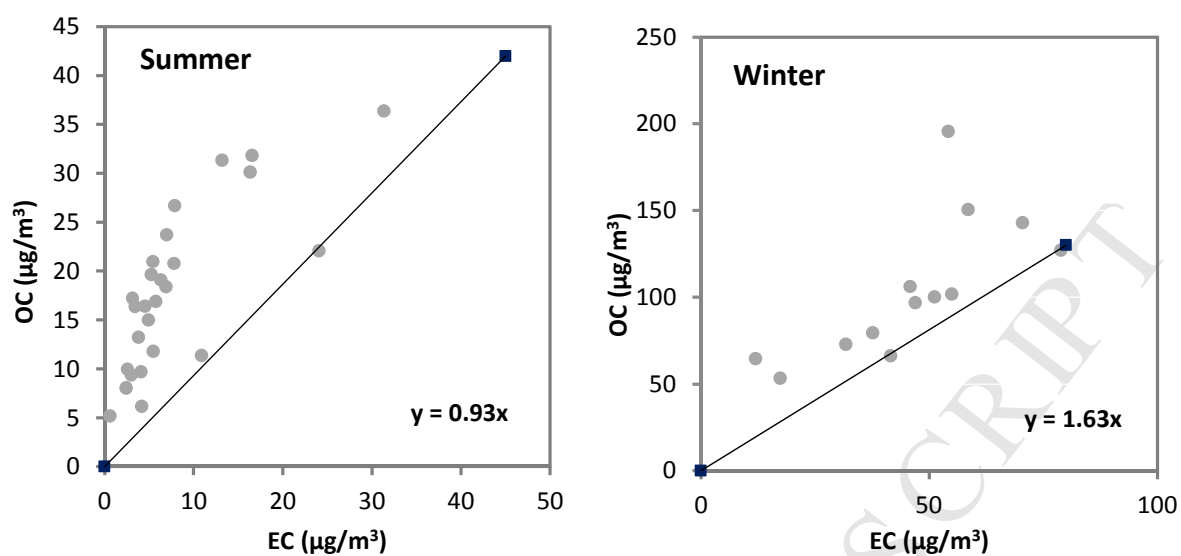


Figure 4: Estimation of minimum OC/EC ratio using the EC tracer method

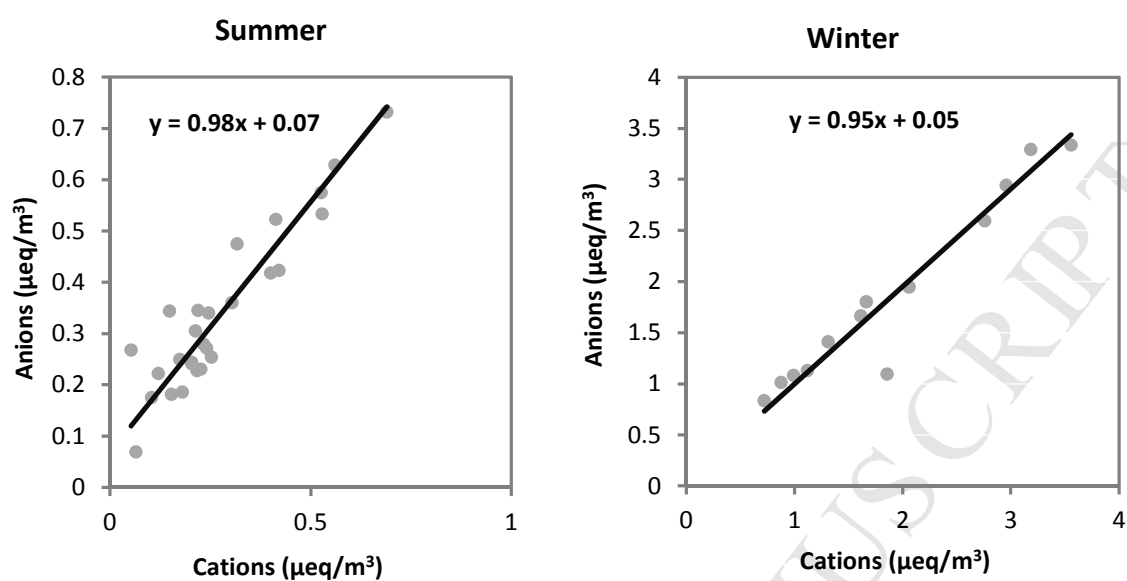


Figure 5: RMA regression between ammonium and sum of anions (i.e. nitrate, sulphate, chloride)

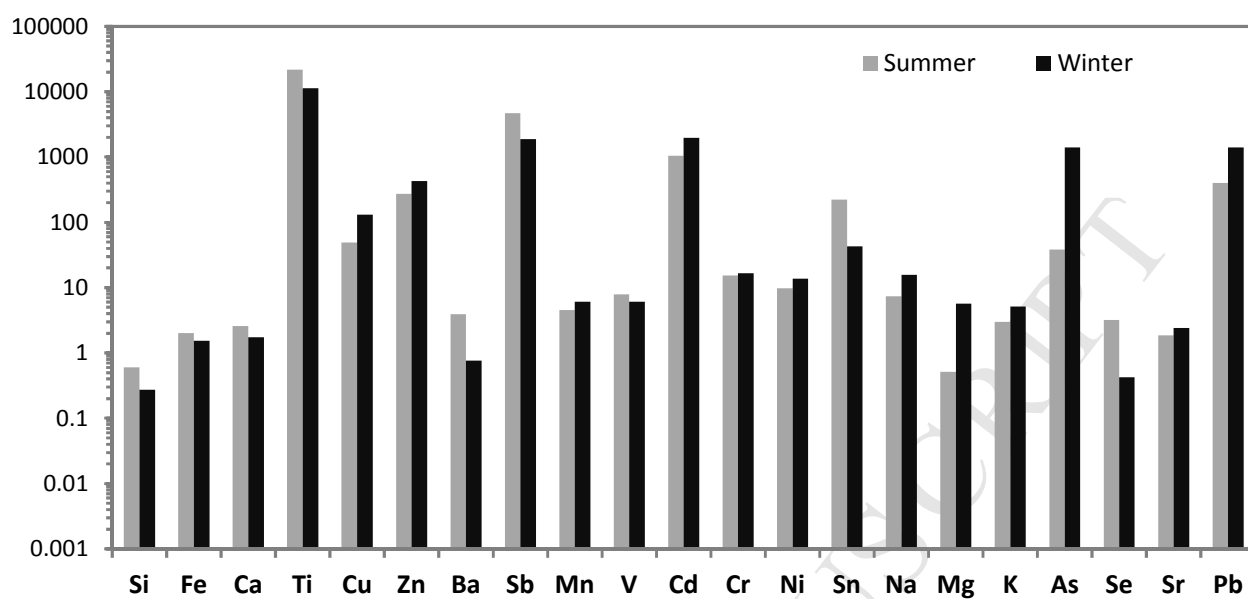
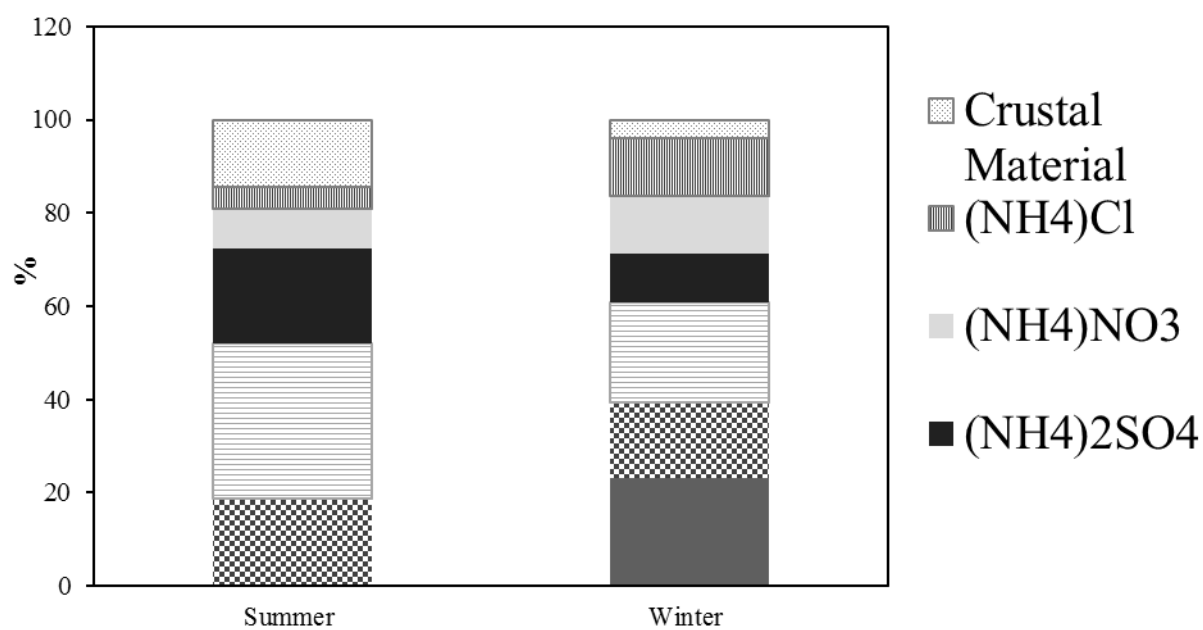


Figure 6: Enrichment factors for select elements



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Figure 7: Mass closure for PM_{2.5} at CRRI

Characterization of Ambient PM_{2.5} at a Pollution Hotspot in New Delhi, India and Inference of Sources

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HIGHLIGHTS

- Chemical composition measured in summer and winter campaigns
- Analyses of many elements, ions, OC/EC and organic molecular markers
- Winter campaign mass concentrations far exceed those in the summer campaign
- Major components (ammonium salts, woodsmoke, traffic, crustal) are quantified
- Good mass closure achieved

SUPPLEMENTARY INFORMATION

Characterization of Ambient PM_{2.5} at a Pollution Hotspot in New Delhi, India and Inference of Sources

Pallavi Pant¹, Anuradha Shukla², Steven D. Kohl³, Judith C. Chow³, John G. Watson³ and Roy M. Harrison

Table S1: Previous studies reporting concentrations of PM_{2.5} at sites in India

Reference	City	Site Type	Measurement Technique	Year	Season	PM _{2.5} concentrations (µg/m ³)
Trivedi et al., (2014)	Delhi	Residential	Beta Attenuation Monitor (BAM), real-time data	2010-2011	Summer	86.4 ± 26.8 (a) 40.6 - 144.7 (r)
					Winter	221.1 ± 94.7 (a) 80.7 - 470.1 (r)
Tiwari et al. (2014)	Delhi	Residential	Beta Attenuation Monitor (BAM), real-time data	2010-2011	Summer	91.0
					Winter	169.4
Saraswat et al. (2014)	Delhi	Various locations	TSI DustTrak 8250 aerosol monitor, real-time data	2010	Spring/Summer	96 - 232 (r)
Bisht et al. (2013)	Delhi	Ten different locations across Delhi	Beta Attenuation Monitor (BAM), real-time data	2010	Post monsoon	112.1 ± 56.0
Singh et al. (2011)	Delhi	Roadside	APM 550 Fine Particle Samper, offline data	2007-2008	Winter	61.8 ± 11.7 (a) 30.92 - 73.5 (r)
					Summer	39.4 ± 13.9 (a) 16.3 - 63.2 (r)
Srimuruganandam and Shiva Nagendra (2012)	Chennai	Urban roadside	Envirotech APM 550 Fine Particle Samper, offline data	2008-2009	Winter	74.1 ± 14.4 (a)
					Summer	67.4 ± 20.2 (a)
Joseph et al. (2012)	Mumbai	Control	AirMetrics Minivol Sampler	2007-2008	Average of summer, winter and monsoon	69 ± 20 (a)
		Kerbside				84 ± 31 (a)
		Industrial				95 ± 36 (a)
		Residential				89 ± 33 (a)

a: mean ± standard deviation; r: range